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INITIATION VIA HALOBORATION IN LIVING CATIONIC POLYMERIZATION. 6. A NOVEL METHOD FOR THE SYNTHESIS OF PRIMARY AMINE FUNCTIONAL POLYISOBUTYLENES

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Key Words: PIB, Telechelic, Haloboration-Initiation, Dichloroborane, Azide, Amine, NMR, FT-IR, Debenzylation, Hydrogenation, Hydrogenolysis

ABSTRACT

Polyisobutylene (PIB) benzyl amine was synthesized by reacting benzyl azide with the dichloroboron head group of PIB obtained by polymerization of isobutylene (IB) via haloboration-initiation with boron trichloride. The facile, one-pot reaction at room temperature resulted in quantitative conversion of the PIB dichloroboron head groups into benzyl amine functionality, determined by ^{1}H NMR spectroscopy and titration with perchloric acid. The hydrogenation of the secondary amine was attempted with various hydrogenation catalysts, of which only palladium yielded primary amine functional PIB. Pt and PtO hydrogenated the benzene ring resulting in PIB cyclohexyl methylene amine. With Pd only about 80% of the chain ends carried the primary amine functional group, apparently due to a side

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reaction. The side reaction was studied by ^{1}H NMR spectroscopy using PIB benzyl amine prepared from deuterated IB. Although direct evidence was not obtained, the ^{1}H NMR spectrum of the debenzylated product indicates that elimination of the amine group from the α carbon and elimination of a methyl group from the β carbon take place simultaneously, presumably due to the crowded nature of the neopentyl-type structure. The primary amine functional PIB was converted into PIB acetyl amide and imide via acylation with acetyl chloride. The products were analyzed by IR, ^{1}H NMR, and ^{13}C NMR spectroscopy.

INTRODUCTION

Amine functional PIBs are valuable intermediates as a result of their high reactivity. However, their synthesis usually involves a multi-step post-polymerization process due to the difficulty of *in-situ* chain end functionalization [1, 2]. Our research group has recently circumvented this difficulty by the end-capping technique using 1,1-diphenylethylene introduced recently in living cationic polymerization [3]. The resultant primary amine functional PIB, however, is sterically somewhat hindered, which may limit its applications.

We have recently reported a one-pot synthesis of secondary amine functional PIB via organoborane chemistry [4]. The method is based on the reaction between an alkyl azide and the dichloro alkylborane head group of the polymer obtained by haloboration-initiation. The successful quantitative end-functionalization has encouraged us to explore the scope of this type of reaction toward primary amine functional polymers.

EXPERIMENTAL

Materials

The materials used for the polymerization and the polymerization conditions have been described elsewhere [4]. Benzyl azide was synthesized according to Reeves *et al*. [5]. The catalysts (palladium, 5 wt% on activated carbon, Aldrich; platinum on powdered charcoal, Matheson Coleman & Bell; platinum oxide, Matheson Coleman & Bell; Raney nickel, 50% slurry in water, Aldrich), Celite 521 (Aldrich), trimethylsilyl azide (97%, Fluka), and triethyl amine (98%, EM Science) were used as received. For the synthesis of acetyl azide a proce-

dure by Agawa *et al.* [6] was adopted. To a solution of 14.2 ml acetyl chloride (98%, Aldrich, used as received) in 50 ml benzene (Aldrich, used as received) cooled to 0°C in an ice bath was added dropwise 13 g sodium azide dissolved in 50 ml deionized water. The reaction mixture was stirred for 0.5 hours, and then allowed to warm to room temperature. The benzene layer was separated, washed with sat. NaCl solution, and dried over anhydrous sodium sulfate. Ethyl azidoformate was synthesized according to the literature [7].

Procedures

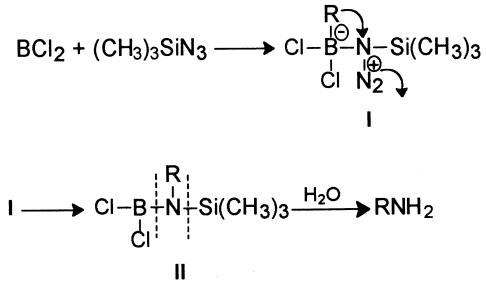
The synthesis of PIB benzyl amine was similar to that of PIB butyl amine [4]. The debenzylation was carried out as follows: A 25 ml flask was charged with 0.1 g catalyst. After the addition of a solution of 0.3 g PIB benzyl amine in 15 ml hexane, the flask was flushed with argon. Hydrogen was bubbled through the stirred reaction mixture for 30 minutes. The reaction mixture was stirred under hydrogen atmosphere overnight, then filtered on a Celite pad, precipitated with methanol three times, and dried.

The acetylation for the synthesis of the amide was carried out by adding 0.1 ml triethyl amine to a solution of 0.4 g PIB in 60 ml hexane, followed by the addition of 0.01 ml acetyl chloride under argon. The reaction mixture was stirred at room temperature for 1 hour, and then the PIB was precipitated with methanol three times.

The synthesis of the imide was similar to that of the amide, except 2 ml triethyl amine and 1 ml acetyl chloride were used.

RESULTS AND DISCUSSION

It is reasonable to depict a synthetic scheme for the preparation of primary amines based on the generalization of the reaction of alky dichloroboranes with alkyl azides. The above reaction gives secondary amines due to the strong covalent bond between the nitrogen and the alkyl carbon in the azide. However, it occurred to us that primary amines could be directly prepared upon rendering this bond susceptible to hydrolytic scission. Despite the lack of similar attempts in the literature we felt encouraged by the simplicity of the scheme and the scope of the reaction, particularly in the synthesis of primary amine functional polymers. We examined various azides with hydrolytically relatively unstable bonds between the nitrogen and the adjacent atom. The first candidate was the com-



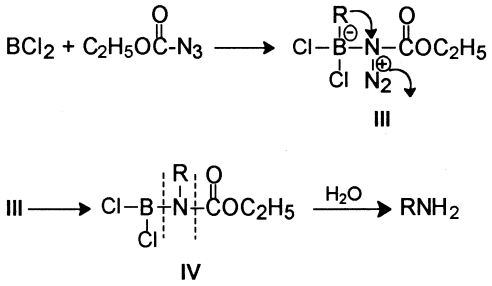
Scheme 1. Hypothetical reaction scheme for the reaction between alkyl dichloroboranes and silyl azide.

mercially available silyl azide. Silicon-nitrogen bonds are known to cleave upon hydrolytic attack. The envisioned reaction is shown in Scheme 1.

The reaction was attempted both at low (-78°C) and room temperature, but even the formation of **II** was not detected. Evolution of N_2 during stirring the reaction mixture was not observed, and the ^{1}H NMR spectrum of the product did not show the presence of an amine. The lack of reactivity of silyl azide toward an alkyl dichloroborane can be explained by steric hindrance or by the difference in the electronic structure of alkyl azides and silyl azide. The lower electronegativity of Si compared to C probably does not result in a sufficiently large positive charge on the β N for the migration of the alkyl group and the elimination of N_2 if **I** forms at all. We have no evidence for the formation of **I**, Si may not support even the reversible formation of the adduct. We cannot exclude the migration of a chloride instead of the alkyl group, as well. However, the investigation of the possible events is beyond the scope of this work.

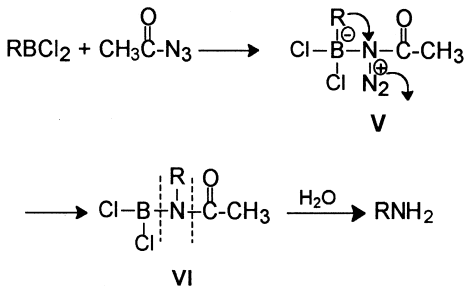
Ethyl azidoformate (Scheme 2) and acetyl azide (Scheme 3) were also counted as potential candidates. The envisioned reaction schemes are similar to the one described above. The N-C bond was expected to support the adduct formation and the alkyl group migration, whereas the presence of the carbonyl group adjacent to the α N would ensure the ready hydrolysis of the N-C bond. Unfortunately, the formation of amine or a derivative thereof, was not detected. This can also be attributed to the electron rich environment attributed to the presence of the carbonyl group.

The failure of azides other than alkyl azides to undergo the reaction with alkyl dichloroboranes suggests that only alkyl azides facilitate the formation of

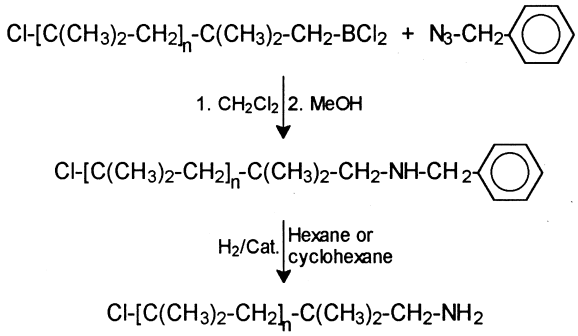


Scheme 2. Hypothetical scheme for the reaction between alkyl dichloroboranes and ethyl azidoformate.

amines under the conditions examined. However, alkyl azides result only in secondary amines, thus the direct synthesis of primary amines can not be accomplished in this type of reaction. Nevertheless, the freedom of choice of the alkyl group in the azide allows us to obtain primary amines by introducing a second step in the reaction scheme: the conversion of a secondary amine into a primary amine. It is well known in organic chemistry that benzyl ethers and amines can be reductively debenzylated into alcohols and amines with lower substitution. The catalytic debenzylation of benzyl amines has been reviewed by Dahn and Solms [8]. It was found that tertiary amines debenzylate into secondary amines 20 times faster than secondary amines into primary amines, but the primary benzylamine does not debenzylate further. Palladium and Raney Ni work well as catalysts, palladium on animal charcoal being the most effective. Platinum is known to induce side reactions, namely hydrogenation of the benzene ring.



Scheme 3. Hypothetical scheme for the reaction between alkyl dichloroboranes and acetyl azide.



Scheme 4. Synthesis of primary amine functional PIB.

Thus, we decided to employ the above method for a convenient synthesis of primary amine functional PIB. The synthetic route is shown in Scheme 4. The synthesis of PIB benzyl amine was similar to the previously reported PIB butyl amine [4], except that benzyl azide was used in place of butyl azide. The reaction is fast (Figure 1), although somewhat slower than with butyl azide.

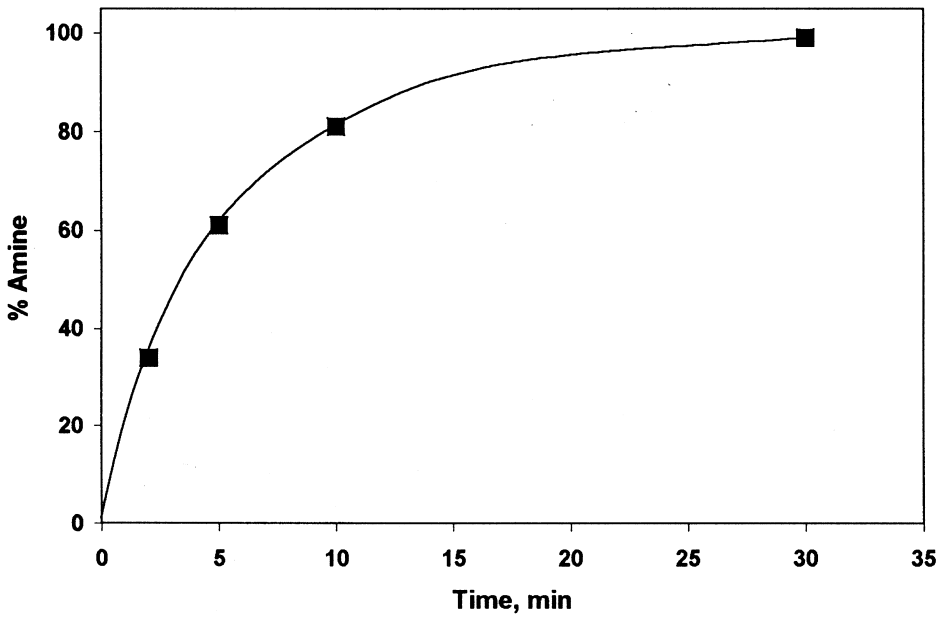


Figure 1. Rate of the formation of PIB benzyl amine in CH_2Cl_2 at room temperature. $[PIB\text{-}BCl_2]_o$=0.032M, $[PhCH_2N_3]_o$=0.101M.

According to the plot, the reaction is complete in 30 minutes under these conditions. However, the concentrations can be further increased, and in turn the reaction can be accelerated.

The ^{1}H and ^{13}C NMR spectra of PIB benzyl amine are shown in Figures 2 and 3, respectively. The presence of the methylene protons adjacent to the nitrogen (2.4 and 3.8 ppm) and the aromatic protons (7.25-7.45 ppm) in the ^{1}H NMR spectrum clearly indicate the formation of the benzyl amine. The characteristic peaks in the ^{13}C spectrum appear at 55.1 ppm, 54.7 ppm, and the aromatic carbons at 141.0, 128.5, 129.3, and 127.2 ppm.

Debenzylation of the PIB benzyl amine was attempted with several hydrogenation catalysts. For the sake of simplicity, we carried out the hydrogenolysis at atmospheric pressure and room temperature. Due to the heterogeneous nature of the catalysis, the rate is proportional to the amount of catalyst.[9] Using 10 mg palladium (5% on charcoal) for 0.3 g of PIB benzyl amine (10^{-4} mole) hydrogenation was not observed in two days. However, 50 mg pal-

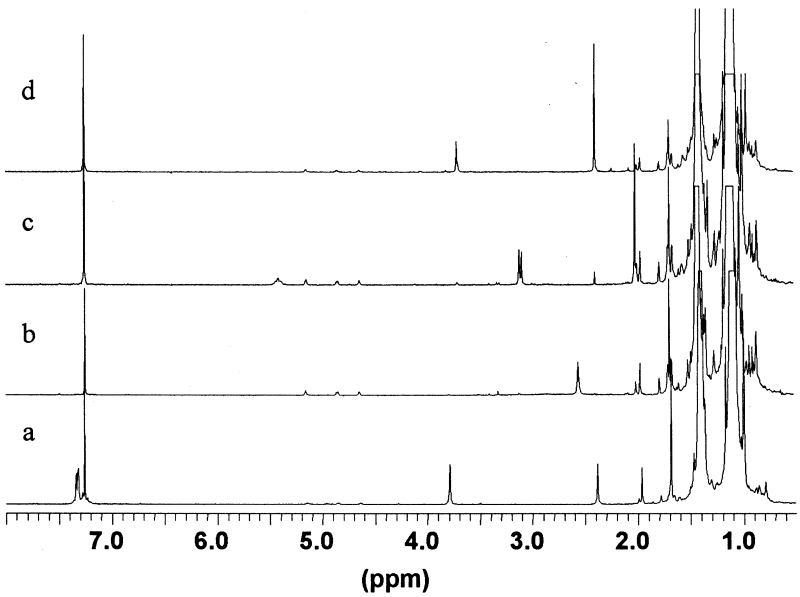


Figure 2. ^{1}H NMR spectra of amine functional PIB and the acetylated derivatives. (a) PIB benzyl amine, (b) PIB primary amine, (c) PIB acetamide, (d) PIB acetimide.

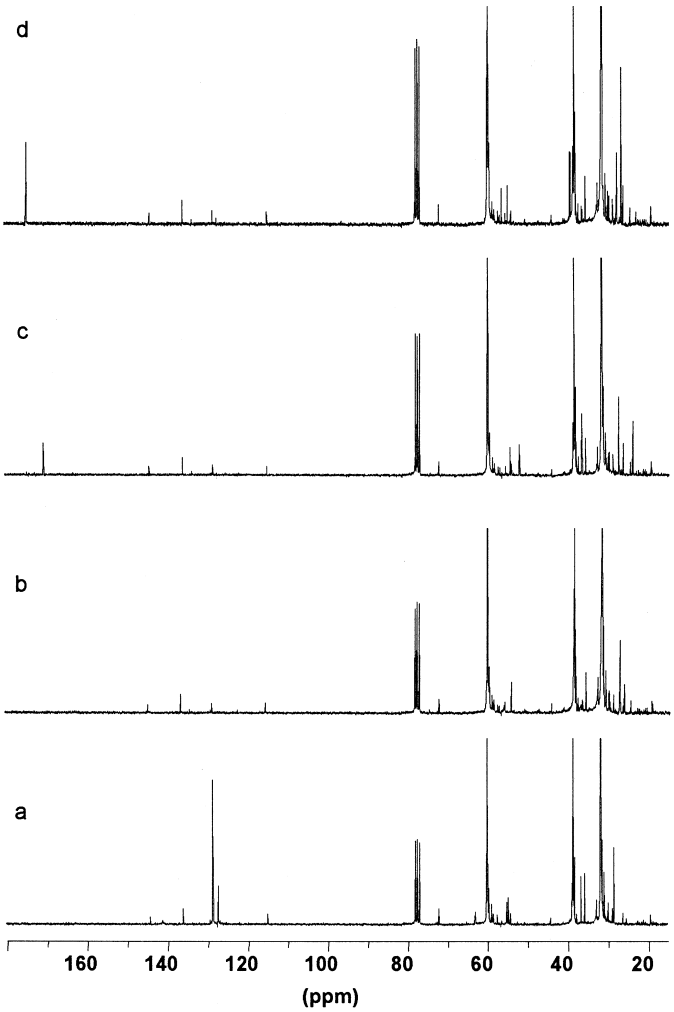


Figure 3. ^{13}C NMR spectra of amine functional PIB and the acetylated derivatives. (a) PIB benzyl amine, (b) PIB primary amine, (c) PIB acetamide, (d) PIB acetimide.

ladium gave 88% primary amine in one day and complete hydrogenolysis in two days. After one day the conversion was complete when 100 mg palladium was used. Gentle heating also accelerated the debenzylation.

The results obtained with different hydrogenation catalysts are shown in Table 1. The relative amounts of the original amine and the hydrogenated products were determined by ^{1}H NMR spectroscopy. The only catalyst that did not

TABLE 1. Results of Hydrogenation of PIB Benzyl Amine with Different Catalysts

Catalyst	g catalyst/ 0.3 g PIB	Time, day	PIB benzyl amine remained (%)	PIB primary amine (%)	PIB methyl cyclohexyl amine (%)
Pd (5% on C)	0.1	1	0	79	0
"	0.05	1	12	68	0
"	0.05	3	0	79	0
"	0.01	2	100	0	0
Pt (5% on C)	0.1	1	29	0	70
"	0.2	1	11	0	89
PtO	0.01	1	61	0	37
"	0.1	1	0	0	100
Raney Ni (50% aqueous slurry)	0.1	1	100	0	0

show activity was Raney Ni. Although it is a commonly used catalyst for hydrogenation, the 50% aqueous slurry is perhaps a too polar medium for PIB (particularly in hexane) to allow adsorption of the polymer on the catalyst. The most active catalyst appears to be PtO. However, the only product seems to be PIB cyclohexyl methylene amine. In addition to the benzene ring, this catalyst hydrogenates the double bonds on the ω chain end, as well. The ^{1}H NMR spectra of the products obtained with the different catalysts are compared in Figure 4.

With Pt and PtO (PtO being the more active catalyst) hydrogenolysis does take place, indicated by the disappearance of methylene peaks adjacent to the amine (recall Figure 2). Two new peaks appear at 2.4-2.5 ppm (a doublet and a singlet) and a very broad peak at 1.5-1.8 ppm, which correspond to the PIB cyclohexyl methylene amine formed upon hydrogenolysis of the ring. The disappearance of the aromatic peaks (7.3-7.4 ppm; the persistent peak at 7.25 ppm is due the presence of chloroform in the deuterated solvent) and the peaks at 4.65, 4.85, and 5.2 ppm (double bonds on the ω chain end) is also noted. With

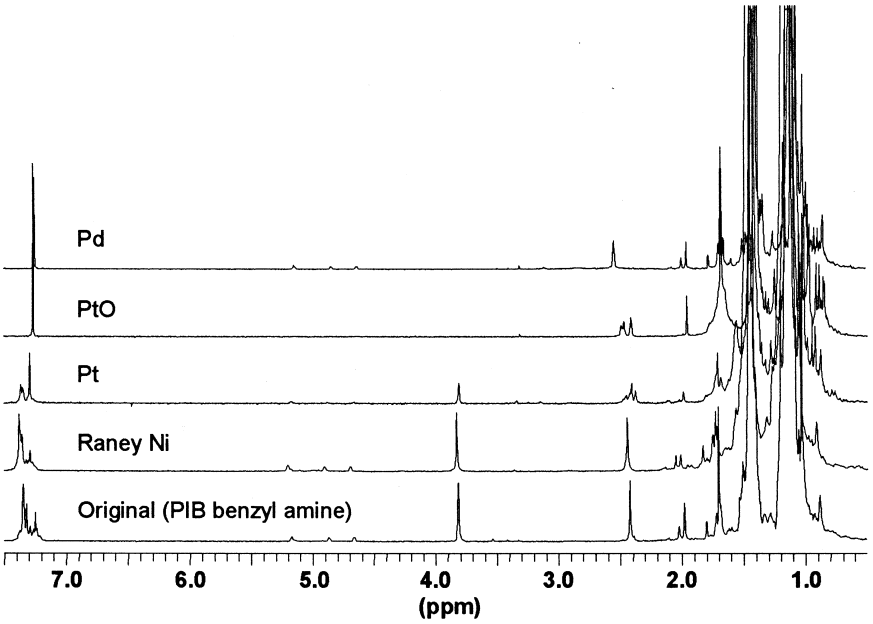


Figure 4. ^{1}H NMR spectra of the products of hydrogenolysis with different catalysts.

palladium, on the other hand, hydrogenation of unsaturated bonds is not observed. However, the primary amine functionality of the product is only 79% by ^{1}H NMR and 58% by titration. This suggests that a side reaction occurred reducing the amount of the amine functional group. This phenomenon was very surprising at the first glance, since hydrogenolysis of benzyl amines is known as a clean synthetic method without any reported side reactions. The most possible side reaction is the elimination of the amine group from the PIB. This could take place in the PIB benzyl amine by the cleavage of the C-N bond on the PIB side of the secondary amine instead of the benzyl side, resulting from the elimination of benzyl amine. This is, however, not very likely due to the much greater stability of the benzyl radical compared to the neopentyl radical. The elimination of the amine nitrogen can also take place from the PIB primary amine, by further hydrogenation with the elimination of ammonia. This would hydrogenate the methylene group bonded to the N into a methyl group. One could also envision a rearrangement of the neopentyl radical by a methyl radical shift. However,

such shift is very unlikely to take place [10]. Such hydrogenation of the PIB primary amine would be very unusual, since even primary benzyl amine does not undergo hydrogenolysis despite the great stability of the benzyl radical. The absence of either of these side reactions was experimentally determined by carrying out the hydrogenation on a PIB benzyl amine synthesized from deuterated PIB. Since these side reactions would be a result of hydrogenation of the PIB methylene carbon – nitrogen bond, the formed neopentyl CD_2H- or the rearrangement product CD_3-CD_2-$CH(CD_3)$- protons could be seen in the ^1H NMR spectrum of the products. These protons were not observed even after five days at 0.1g catalyst/0.3 g PIB benzyl amine. The chemical shifts of these peaks were calculated using the ACD NMR software (Advanced Chemistry Development Inc., Toronto, Canada). The former proton would have a chemical shift of 0.91 ppm and a multiplicity of 5. The latter proton, which corresponds to the rearranged product, would appear at 1.47 ppm with a multiplicity of 15. The high multiplicity is a result of the neighboring deuteriums. The actual ^1H NMR spectrum of the hydrogenolysis product is compared with that of the deuterated PIB benzyl amine in Figure 5. Apparently, the debenzylation is complete, as indicated by the disappearance of the peak at 3.8 ppm (Ph-C<u>H</u>$_2$-NH-).

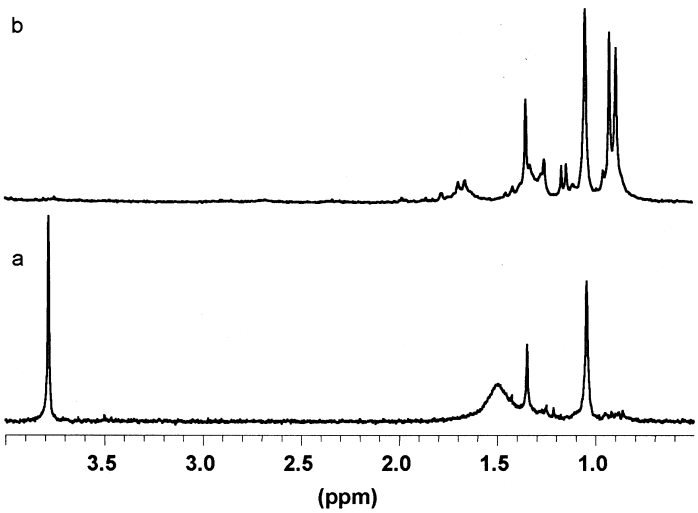


Figure 5. ^1H NMR spectra of deuterated PIB benzyl amine (a) before and (b) after hydrogenolysis.

The new peaks, however, are a doublet at 0.9 ppm, a doublet at 1.15 ppm, and a multiplet at 1.55-1.75 ppm. The doublet at 0.9 ppm appears to be a methyl peak and can be rationalized as the product of the elimination of a CD_3 group from the β carbon and that of ammonia from the α carbon due to hydrogenation of the corresponding bonds ($C\underline{H}_3$-$CH(CD_3)$-CD_2-). The low multiplicity of the peak can be explained by a fast exchange between deuteriums and protons on the carbon adjacent to the nitrogen with protons replacing all the deuteriums. The multiplet at 1.55-1.75 ppm could be assigned to the methine proton (CH_3-$C\underline{H}(CD_3)$-CD_2-) in accordance with the above described side reaction.

We attempted to compare the rate of the side reaction with the rate of debenzylation. For this, the hydrogenolysis was carried out in cyclohexane at three different temperatures with 0.1 g catalyst/0.3 g PIB. The amount of primary amine continuously increases at the expense of the secondary amine chain ends, until the debenzylation is almost complete after 24 hours. However, the total amine decreases to ca. 80% shortly after the hydrogenolysis is started and practically remains unchanged. At higher temperatures the debenzylation is much faster, but the total amine content is only about 80% and does not change any further after the beginning of the reaction. This is surprising, since a side reaction, similar to the one hypothesized above, should take place continuously throughout the entire course of the debenzylation. The molecular weight of the sample did not change during debenzylation, thus intermolecular reaction is probably absent.

The reactivity of the primary amine functional PIB was tested by acylation of the amine with acetyl chloride. The sample readily underwent complete acylation in hexane at room temperature in one hour. When acetyl chloride was used in small excess, acetyl amide formed. The ^{1}H and the ^{13}C NMR spectra are shown in Figures 2 and 3, respectively. However, when a large excess of acetyl chloride was added to the amine, the corresponding imide formed. The products were also analyzed by FT-IR spectroscopy. The spectra are compared in Figure 6. Aliphatic primary amines show two weak absorption bands at 3500 cm^{-1} and 3400 cm^{-1} (N-H stretching), a medium band at 1650-1580 cm^{-1} (N-H bending), and a weak band at 1250-1020 cm^{-1}. The concentration of the amine group in the end-functional PIB is very low, thus the relative intensity of weak absorption bands falls below the detection limit in the infrared spectrum. On the other hand, the C=O stretching vibration in amides results in a strong absorption band at 1640 cm^{-1} (amide I band), which appears in the spectrum of the acetyl amide. The amide II band of secondary amides (N-H bending) appears in the region 1570-1515 cm^{-1}, and its intensity is one-half to one-third of the amide I band. In

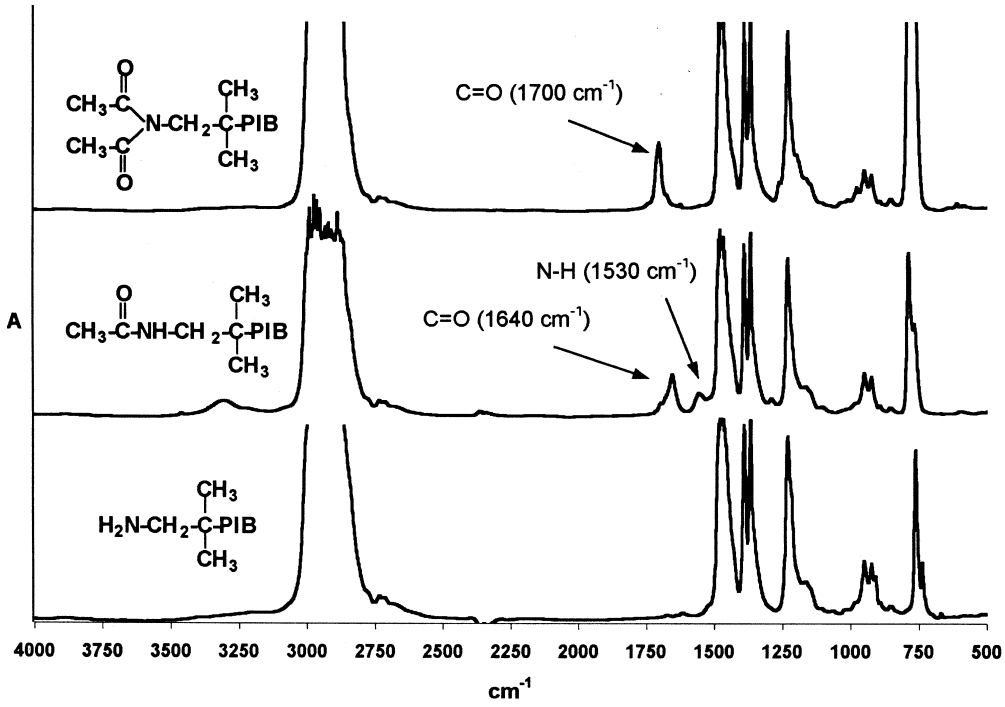


Figure 6. FT-IR spectra of derivatives of primary amine functional PIB.

the spectrum of the PIB acetyl amide, it appears at 1530 cm^{-1} with intensity half of that of the carbonyl stretching band. In the spectrum of the imide, the carbonyl absorption shifts to 1700 cm^{-1}. Due to the lack of N-H bending, imides do not show the amide II band, whose absence can be seen in Figure 6 when the spectra of the amide and the imide are compared. These results are in excellent agreement with those obtained by NMR spectroscopy.

The calculated and experimental chemical shifts of the amine functional PIB derivatives are listed in Table 2. The calculations were carried out using ACD HNMR 1.0 and ACD CNMR 1.1 programs.

CONCLUSION

Primary amine functional PIB can be obtained via the facile synthesis of PIB benzyl amine, followed by catalytic hydrogenolysis. A formerly unreported

TABLE 2. ^{1}H and ^{13}C NMR Chemical Shifts of Amine Functional PIB Derivatives

Derivative	Nucleus	Chemical Shifts, ppm	
		Calculated	Experimental
PIB Benzyl Amine	$PhC\underline{H}_2NH$-	3.57±0.2	3.79
	-NH-$C\underline{H}_2$-$C(CH_3)_2$-PIB	2.76±1.0	2.38
	$PhC\underline{C}H_2NH$-	53.93±0.7	55.08
	-NH-$C\underline{C}H_2$-$C(CH_3)_2$-PIB	60.00±4	54.70
	Ph-; C1	138.53±2	141.02
	Ph-; C2, C6	127.22±1.2	128.5
	Ph-; C3, C5	128.37±0.4	129.3
	Ph-; C4	126.8±0.4	127.2
PIB Primary Amine	H_2N-$C\underline{H}_2$-$C(CH_3)_2$-PIB	2.54±0.9	2.55
	H_2N-$C\underline{C}H_2$-$C(CH_3)_2$-PIB	53.27±5.1	54.14
PIB Acetyl Amide	$C\underline{H}_3CONH$-	1.89±0.3	1.99
	-NH-$C\underline{H}_2$-$C(CH_3)_2$-PIB	3.02±0.3	3.10
	$C\underline{C}H_3CONH$-	22.91±1.4	24.0
	$CH_3\underline{C}ONH$-	172.55±5.8	170.4
	-NH-$C\underline{C}H_2$-$C(CH_3)_2$-PIB	52.47±3.5	52.2
PIB Acetyl Imide	$(C\underline{H}_3CO)_2N$-	1.91±0.11	2.39
	-N-$C\underline{H}_2$-$C(CH_3)_2$-PIB	3.29±0.3	3.71
	$(\underline{C}H_3CO)_2N$-	26.12±2.5	26.9
	$(CH_3\underline{C}O)_2N$-	173.5±3.1	174.6
	-N-$C\underline{C}H_2$-$C(CH_3)_2$-PIB	57.07±18.2	56.4

side reaction results in a ~20% loss of amine functionality. Studies carried out with a deuterated PIB derivative suggests that the side reaction involves the simultaneous elimination of the terminal amine group and that of a methyl group from the β carbon. This type of side reaction, not yet reported in the literature, would probably not take place with sterically less hindered amines.

Consequently, the technique could presumably be applied for the quantitative synthesis of primary amine functional polystyrene.

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